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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :  C23F 11/14	A1	(11) International Publication Number: WO 93/07307  (43) International Publication Date: 15 April 1993 (15.04.93)
(21) International Application Number: PCT/US92/08036  (22) International Filing Date: 23 September 1992 (23.09.92)		(81) Designated States: CA, JP, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE).
(30) Priority data: 07/774,002 30 September 1991 (30.09.91) US 07/942,242 9 September 1992 (09.09.92) US		Published <i>With international search report.</i>
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(54) Title: DERIVATIVES OF POLYALKYLENEPOLYAMINES AS CORROSION INHIBITORS

## (57) Abstract

A composition of polyalkylenepolyamine derivatives useful as a corrosion inhibitor in aqueous media produced by reacting a starting polyalkylenepolyamine composition comprising a mixture of: (i) at least one C-alkyl-ethylene diamine; and (ii) at least one di-(C-alkyl)-diethylenetriamine; wherein each C-alkyl group on the ethylene diamine and diethylenetriamine independently contain between 8-26 carbon atoms; with a derivatizing agent which is either an alkylating agent or an alkylene oxide. Methods for preparing this composition and using it to inhibit the corrosion of corrodible metal alloys are also disclosed.

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1                   DERIVATIVES OF POLYALKYLENEPOLYAMINES  
2                   AS CORROSION INHIBITORS

3

4                   BACKGROUND OF THE INVENTION

5

6   This invention relates to compositions comprising  
7   polyalkylenepolyamine derivatives which demonstrate  
8   improved properties as corrosion inhibitors when used in  
9   substantially aqueous media. This invention further  
10   concerns a method of making compositions of these  
11   water-soluble, polyalkylenepolyamine derivatives by  
12   reacting a hydrocarbon-soluble polyalkylenepolyamine  
13   composition with either an alkylating agent or an alkylene  
14   oxide. Additionally, this invention also relates to  
15   methods for using the polyalkylenepolyamine derivatives as  
16   effective corrosion inhibitors capable of protecting metal  
17   surfaces placed in contact with potentially corrosive  
18   chemicals.

19

20   Increasingly, industrial companies have begun to realize  
21   the economic importance of maintaining their equipment to  
22   ensure the longest operating life possible. This has been  
23   particularly true in the area of oil field operations.

24

25   As oil companies have been forced to go to new lengths in  
26   their search for oil, their operating equipment has also  
27   become more expensive and difficult to easily replace.

28

29   Given this level of investment, most companies have  
30   increasingly sought to rely on corrosion inhibitors to  
31   protect the metal surfaces on their drilling rigs and  
32   pipelines from the corrosive effects of the chemicals  
33   found in underground environments.

34

35   These corrosion inhibitors can either be applied directly  
36   to the potentially affected metal parts or injected into  
37   the oil well containing the corrosive chemicals. To

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1 achieve maximum effectiveness, the corrosion inhibitors  
2 should be dispersible or miscible in this underground  
3 medium.

4

5 Historically, alkylamines or polyamines have been the most  
6 commonly used corrosion inhibitors in oil well operations.  
7 A recent invention has also created compositions of  
8 polyalkylenepolyamines which are purported to possess even  
9 better corrosion inhibition properties. These chemical  
10 compositions are hydrocarbon-soluble, however, and  
11 experience in the field has shown that they are of limited  
12 effectiveness in the substantially aqueous environments  
13 one can potentially confront when drilling for oil. Since  
14 the base amines of these compositions are insoluble in an  
15 aqueous medium, they simply cannot work to maximum  
16 effectiveness as corrosion inhibitors in water-based  
17 environments.

18

19 The instant invention offers the ability to solve this  
20 limitation presently hampering these types of corrosion  
21 inhibitors. It proposes methods for the derivatization of  
22 polyalkylenepolyamine compositions into novel compositions  
23 of derivatized polyalkylenepolyamines.

24

25 These novel chemical compositions demonstrate increased  
26 water solubility, making them more effective in the  
27 heavily aqueous corrosive media, which are increasingly  
28 encountered in the ever-expanding search for new sources  
29 of oil.

30

31 In traditional oil production operations, the drilling  
32 rods are introduced into a subsurface environment largely  
33 consisting of hydrocarbon compounds. While some water is  
34 theoretically present in all wells, the corrosion and  
35 pitting which occur in these situations are largely the  
36 result of the effects of the hydrocarbon compounds on the  
37 rod. As noted previously, to achieve maximum

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1 effectiveness, a corrosion inhibitor should be dispersible  
2 in the medium in which it is to operate. Thus, the  
3 standard hydrocarbon-soluble amine or  
4 polyalkylenepolyamine composition provides adequate  
5 coverage in most "typical" oil production operations.

6

7 Increasingly, however, as our domestic supply of oil  
8 continues to dwindle, many oil companies are being forced  
9 to expand their quest for this valuable resource into many  
10 non-traditional areas. For example, a large percentage of  
11 the new wells being drilled are in substantially aqueous  
12 environments, presenting an even greater need to monitor  
13 the effects of corrosion on operating efficiency.

14

15 Numerous experiments have repeatedly demonstrated that the  
16 presence of water in underground environments greatly  
17 speeds up pitting and corrosion processes. Many new wells  
18 are affected by CO<sub>2</sub> corrosion resulting from the carbonic  
19 acid which forms when CO<sub>2</sub> comes in contact with water.

20 Additionally, oxygen entering a heavily aqueous well also  
21 reacts with water in a manner that speeds up the effects  
22 of corrosion. Thus, it is especially vital to use  
23 effective corrosion inhibitors when operating in  
24 substantially aqueous media in order to counteract the  
25 added threat of corrosion in this type of environment.

26

27 Unfortunately, base amines and their more specialized  
28 polyalkylenepolyamine counterparts have not proven  
29 effective in these situations. Because most of these  
30 compounds are highly insoluble in water, when they are  
31 applied to drilling rods being used in substantially  
32 aqueous environments, they have shown a tendency to  
33 migrate from water, which is usually the layer in direct  
34 contact with the drilling rods, and dissolve in the  
35 hydrocarbon layer. With no protection between the  
36 dangerous aqueous layer and the drilling rod, corrosion  
37 proceeds relatively unabated.

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1 Many in industry have attempted to solve this problem by  
2 searching for corrosion inhibitors which are dispersible  
3 in water, and thus effective in heavily aqueous media.  
4 The instant invention represents a successful culmination  
5 of one individual's efforts in this regard.

6

7 Numerous patents describe polyalkylenepolyamine compounds,  
8 their derivatives, and the processes for their production.

9

10 U.S. Patent No. 4,314,083 discloses a process for  
11 selectively preparing non-cyclic polyalkylenepolyamine  
12 compounds by reacting an alkylenepolyamine compound with a  
13 hydroxy compound in the presence of a catalytically  
14 effective amount of salt, nitrogen, or sulfur-containing  
15 substance. This process is limited to short-chain alkyl  
16 groups consisting of no more than 4 carbon atoms.

17

18 U.S. Patent No. 3,565,941 discloses a process for  
19 alkylating a polyalkylenepolyamine by first reacting the  
20 polyamine with an acid and then following with either an  
21 alkylating agent or a polyamine salt. This process is  
22 also specifically limited to hydrogen or short-chain alkyl  
23 groups of methyl or ethyl. The products also have limited  
24 uses as chemical intermediates, monomers, bases and  
25 flocculating agents.

26

27 Various other amine compounds have been recognized by the  
28 scientific community as effective in minimizing the  
29 corrosion of metal alloys. Prior patents disclose  
30 numerous quaternary, rosin and fatty amine compounds, as  
31 well as their corresponding derivatives, all of which are  
32 considered to be most beneficial in specific types of  
33 industrial operations. Alkylamines and polyamines are  
34 also accepted as particularly effective corrosion  
35 inhibitors in oil field operations. For years, however,  
36 researchers have been attempting to further refine these  
37 compounds in the hopes of developing other compositions

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1 which demonstrate even better corrosion inhibition  
2 properties.

3

4 U.S. Patent No. 4,900,458, which is incorporated by  
5 reference in its entirety herein, represents a major  
6 success in this regard. Here, Schroeder et al. discovered  
7 methods for manufacturing novel polyalkylenepolyamine  
8 compositions in which an alkyl group of between 10-28  
9 hydrocarbons was attached to the carbon atom instead of  
10 the nitrogen. This structural modification was shown to  
11 enable these hydrocarbon-soluble compositions to exhibit  
12 improved corrosion inhibition properties in oily media.

13

14 In contrast, the present invention provides excellent  
15 corrosion inhibitors useful in substantially aqueous  
16 media.

17

18 SUMMARY OF THE INVENTION

19

20 The instant invention relies upon the  
21 polyalkylenepolyamine compositions of U.S. Patent No.  
22 4,900,458 as its starting material. These compositions  
23 are reacted with either an alkylene oxide or an alkylating  
24 agent to yield highly water-soluble or dispersible  
25 derivatives of polyalkylenepolyamines. These derivatives  
26 demonstrate surprisingly improved abilities as corrosion  
27 inhibitors when used in aqueous media, far surpassing the  
28 results obtained by known basic amine inhibitors or the  
29 more specialized polyalkylenepolyamine starting materials  
30 referred to above.

31

32 This invention provides compositions of  
33 polyalkylenepolyamine derivatives which offer improved  
34 corrosion inhibition properties when used in substantially  
35 aqueous media. Specifically, but without limitation,  
36 these compositions are uniquely effective in certain  
37 operations involving the production and transportation of

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1 oil. In a preferred embodiment, the amine groups of the  
2 polyalkylenepolyamines are methylated prior to  
3 derivatization, with for example an alkyl halide or a  
4 dialkyl sulfate.

5

6 The instant invention provides a substantially  
7 water-soluble, corrosion-inhibiting, composition of  
8 polyalkylenepolyamine derivatives. This composition is  
9 obtained by reacting a mixture containing: (i) at least  
10 one C-alkyl-ethylene diamine and (ii) at least one  
11 di-(C-alkyl)-diethylenetriamine; wherein each C-alkyl  
12 group on the ethylene diamine and diethylenetriamine  
13 independently contains from 8-26 carbon atoms, with  
14 specially selected alkylating agents or an alkylene oxide,  
15 preferably ethylene oxide. In a preferred embodiment, the  
16 amine groups of the polyalkylenepolyamines are methylated  
17 prior to derivatization, with for example, an alkyl halide  
18 or a dialkyl sulfate.

19

20 The instant invention also relates to a method of  
21 inhibiting corrosion on corrodible metals by directly  
22 applying the derivatized polyalkylenepolyamine composition  
23 to the potentially affected metal.

24

25 The instant invention also has specific applications in  
26 the oil production industry. It encompasses a method for  
27 inhibiting corrosion on corrodible metals used in or  
28 around substantially aqueous oil wells which involves  
29 injecting the composition of polyalkylenepolyamine  
30 derivatives directly into the underground oil well  
31 environment.

32

33 Among other factors, the instant invention is based on our  
34 discovery that a mixture of derivatized C-alkyl-ethylene  
35 diamines and di-(C-alkyl)-diethylenetriamines, wherein  
36 each alkyl group independently contains from 8-26 carbon  
37 atoms, demonstrate excellent corrosion inhibition

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1 potential in substantially aqueous media. Because these  
2 derivatized polyalkylenepolyamine mixtures are water  
3 dispersible, they give at least 85% inhibition of CO<sub>2</sub>  
4 corrosion, and preferably greater than 90% inhibition, in  
5 the industry-standard wheel test with NACE brine.  
6 Preferred compositions are effective in the 250 to 25 ppm  
7 concentration range.

8

9                   DETAILED DESCRIPTION OF THE PREFERRED  
10                  EMBODIMENTS OF THE INVENTION

11

12 The instant invention provides a water-soluble composition  
13 of polyalkylenepolyamine derivatives which exhibit  
14 excellent corrosion inhibition properties when used in  
15 substantially aqueous media. The instant invention  
16 further discloses methods of producing derivatized  
17 compounds by reacting specific polyalkylenepolyamine  
18 compounds with specially selected alkylating agents or  
19 alkylene oxides. Useful alkylating agents are those that  
20 react with primary, secondary or tertiary amines to make  
21 ammonium salts.

22

23 The terms "heavily aqueous" and "substantially aqueous"  
24 are used extensively and interchangeably throughout this  
25 application. As referred to herein, these terms are used  
26 to describe an environment that consists of more water  
27 than hydrocarbons. Preferably this ratio will be greater  
28 than 3 parts water to 1 part oil.

29

30 The specific derivatized compounds which are intended to  
31 be covered by this application are referred to as being  
32 either "soluble" or "dispersible" in water. Preferably,  
33 these compounds will possess a water dispersibility rating  
34 under 10 rating units, as measured by a Water  
35 Dispersibility Test using NACE brine as discussed in  
36 detail in Example 12. Ratings lower than 10 also reflect

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formulations which have a partition coefficient between water and octyl alcohol  $\leq 2$ .

3

4 As used herein, the terms "reaction" or "reacting" shall  
5 be taken to mean a chemical change that occurs by  
6 combination, replacement, decomposition or some  
7 modification thereof.

8

9 As used herein, the term "derivatized" shall be taken to  
10 mean the reaction of at least one of the  
11 polyalkylenepolyamine nitrogens with an alkylating or  
12 alkoxylation agent, i.e., with a derivatizing agent. When  
13 more than one of the nitrogens of a polyalkylenepolyamine  
14 structure are reacted with an alkylating or alkoxylation  
15 agent, the product is termed herein as "polyderivatized."

16

## 17 The Starting Polyalkylenepolyamines

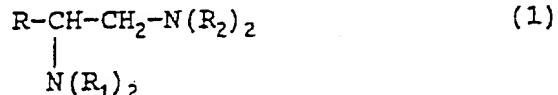
18

19 Polyalkylenepolyamine compounds that can be used to  
20 produce my derivatized compositions are disclosed in  
21 detail in U.S. Patent No. 4,900,458. The instant  
22 invention directly incorporates by reference the specific  
23 chemical compositions and their methods of preparation as  
24 described in detail therein.

25

26 The polyalkylenepolyamine compositions which provide the  
27 foundation for the instant invention contain a mixture of  
28 compounds. This mixture includes at least one  
29 C-alkyl-ethylene diamine as described in Structure 1  
30 below.

31



35

36 In Structure 1, R is an alkyl group containing 8 to 26  
37 carbon atoms.  $R_1$  and  $R_2$  individually can be any

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1 combination of hydrogen or lower alkyl groups. The terms  
2 "lower alkyl" and "lower alkyl group" mean alkyl groups  
3 from 1 to 5 carbon atoms, more preferably methyl or ethyl.  
4 Preferred compositions include those where the R group  
5 contains between 10 and 22 carbon atoms, preferably  
6 between 10 and 16, more preferably 12 and/or 14 carbon  
7 atoms; and where at least one of the R<sub>1</sub> or R<sub>2</sub> groups are  
8 lower alkyl, preferably where a plurality of these R  
9 groups are lower alkyl.

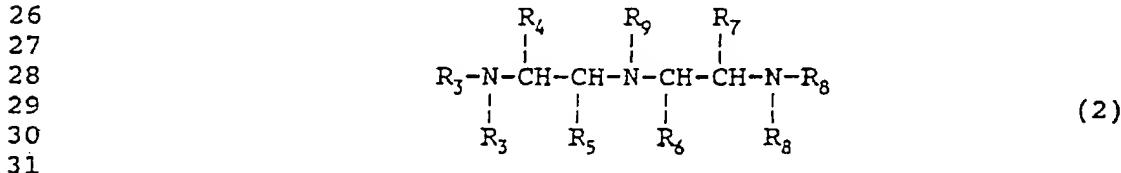
10

11 The starting polyalkylenepolyamines can be made from alpha  
12 olefins via epoxidation and reaction with amines, for  
13 example ammonia, in the presence of an amination catalyst.  
14 For example, see U.S. Patent No. 4,900,458. To clarify  
15 the nomenclature used herein: a C<sub>14</sub> alpha olefin produces  
16 a C<sub>14</sub> epoxide which in turn produces a C<sub>14</sub>  
17 polyalkylenepolyamine. The C<sub>14</sub> epoxide has an alkyl group  
18 of 12 carbon atoms on the epoxide ring and this produces  
19 polyalkylenepolyamines with alkyl groups of 12 carbon  
20 atoms.

21

22 The starting polyalkylenepolyamine composition also  
23 contains at least one di-(C-alkyl)-diethylenetriamine as  
24 detailed in Structure 2 below.

25



32 In Structure 2, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> individually may be  
33 hydrogen or alkyl of 8 to 26 carbon atoms, provided that  
34 two of the R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> groups are hydrogen and two are  
35 alkyl. In Structure 2, R<sub>3</sub>, R<sub>8</sub> and R<sub>9</sub> can individually be  
36 any combination of hydrogen and lower alkyl groups, as  
37 described above. Methods of preparing compounds of  
38 Structure 1 when R<sub>1</sub> and R<sub>2</sub> comprise methyl or compounds of

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1 Structure 2 when R<sub>3</sub>, R<sub>8</sub> and R<sub>9</sub> comprise methyl are  
2 disclosed in Examples 1C, 1D, and 1E, below.

3

4 In a preferred embodiment, reaction of an amine hydrogen  
5 (i.e., N-H) with formic acid and formaldehyde results in  
6 an N-methylated amine, where the N-H group has been  
7 converted to an N-CH<sub>3</sub> group. When there is more than one  
8 N-H group in a molecule (such as in the polyalkylene  
9 polyamines of U.S. Patent No. 4,900,458) reaction with  
10 formic acid and formaldehyde will partially or totally  
11 convert all the N-H groups to N-CH<sub>3</sub> groups, depending on  
12 the reaction conditions and amounts of reactants.

13 Substantially complete conversion is preferred. Another  
14 method of preparing compounds where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>8</sub> and/or R<sub>9</sub>  
15 are lower alkyl is to use alkyl amines, such as methyl  
16 amine or dimethyl amine, instead of ammonia in the  
17 preparation procedures disclosed in U.S. Pat. No.  
18 4,900,458 for the starting polyalkylenepolyamines.

19

20 As used herein, the term "N-methylated"  
21 polyalkylenepolyamines refers to the above-described  
22 polyalkylenepolyamines having one or two methyl groups on  
23 some or all of the amine nitrogens. When there are two  
24 methyl (or lower alkyl) groups on the nitrogen, alkylation  
25 -- for example with an alkyl halide -- results in a  
26 quaternary amine salt (a "quat") having a total of four  
27 alkyl groups on the nitrogen. These N-methylated  
28 polyalkylenepolyamines are useful as corrosion inhibitors  
29 in their own right, and are especially preferred  
30 compositions for preparing the polyalkylenepolyamine  
31 derivatives of this invention. These N-methylated  
32 polyalkylenepolyamines are preferred in part because of  
33 their lower meltpoints, as measured by differential  
34 scanning calorimetry. Lower meltpoints are economically  
35 advantageous in that less heat is required to melt the  
36 polyalkylenepolyamines prior to derivatization or  
37 formulation. Also, these N-methylated

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1 polyalkylenepolyamines are easier to apply in corrosion  
2 applications.

3

4 The terms "C-alkyl" and "di-(C-alkyl)" are also used at  
5 numerous points throughout this application. "C-alkyl" is  
6 meant to encompass any alkyl group that is directly bonded  
7 to a carbon atom in Structure 1, i.e. the R group.  
8 "Di-(C-alkyl)" refers to two alkyl groups which are each  
9 directly bonded to two different carbon atoms in Structure  
10 2, i.e., two of the groups at R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, or R<sub>7</sub>.

11

12 Preparation of Polyalkylenepolyamine Derivatives

13

14 The water-soluble or water-dispersible  
15 polyalkylenepolyamine derivatives which are the subject of  
16 the instant invention are prepared by reacting the  
17 polyalkylenepolyamine mixtures of Structures 1 and 2 with  
18 various alkylating agents or alkylene oxides. Two  
19 preferred methods of preparation are outlined below.

20

21 1. Alkylation of the Polyalkylenepolyamines

22

23 A preferred method for obtaining derivatives of  
24 polyalkylenepolyamines is to react a polyalkylenepolyamine  
25 mixture containing Structure 1 and Structure 2 with an  
26 alkylating agent, BX. In this process, alkylation can  
27 occur on any single nitrogen, all the nitrogen centers, or  
28 any combination thereof. The derivatized versions of  
29 Structures 1 and 2 resulting from this reaction are shown  
30 in Structures 3 and 4, respectively.

31

32 The starting polyalkylenepolyamines can also be N-  
33 methylated by reaction with formic acid and formaldehyde  
34 as described in Examples 1C, 1D, 1E and 1F. These N-  
35 methylated products can then be alkylated to produce  
36 quaternary amine salts of this invention.

37

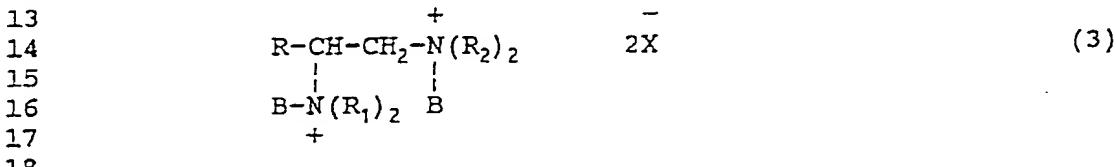
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1 The derivatized water-soluble polyalkylenepolyamine  
 2 composition consists of a mixture containing: (a) at  
 3 least one derivatized C-alkyl-ethylene diamine as  
 4 described in Structure 3 and (b) at least one derivatized  
 5 di-(C-alkyl)-diethylenetriamine as described in Structure  
 6 4. Each C-alkyl group in the derivatized ethylene diamine  
 7 and diethylenetriamine independently contains from 8-26  
 8 carbon atoms.

9

10 The derivatized C-alkyl-ethylene diamine is an ammonium  
 11 salt described by Structure 3 below.

12

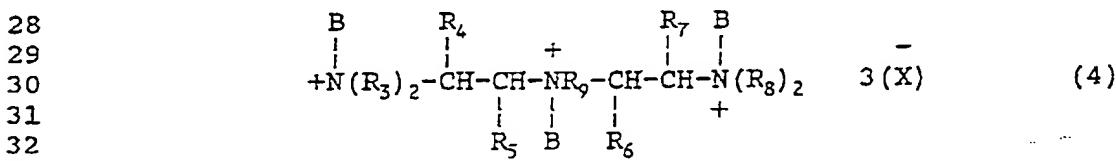


19 In Structure 3, R is an alkyl group containing 8 to 26  
 20 carbon atoms. R<sub>1</sub> and R<sub>2</sub> individually can be hydrogen,  
 21 lower alkyl, or any combination thereof. B is derived  
 22 from the alkylating agent. Polyammonium salts having all  
 23 the amine nitrogens alkylated are preferred.

24

25 A preferred derivatized di-(C-alkyl)-diethylenetriamine  
 26 ammonium salt is described by Structure 4 below.

27



35 In Structure 4, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> individually can be  
 36 hydrogen or alkyl of 8 to 26 carbon atoms, provided that  
 37 two of the R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> groups are hydrogen and two are  
 38 alkyl. R<sub>3</sub>, R<sub>8</sub> and R<sub>9</sub> can individually be any combination  
 39 of hydrogen and lower alkyl groups. B is derived from the  
 40 alkylating agent as described below. Polyammonium salts  
 41 having all the amine nitrogens alkylated are preferred.

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1 In both derivatized structures, the alkylating agent's  
2 alkyl group, B, can be an alkyl or aryl group, benzyl or  
3 alkylcarboxylate. Preferred alkyl groups are methyl,  
4 ethyl and benzyl. The anion, X, can be a halogen,  
5 including chloride, bromide and iodide, a sulfate, such as  
6 O-SO<sub>3</sub>-R or an equivalent anion which is readily displaced  
7 by the nucleophilic nitrogen of the amine. These types of  
8 anions are well known to those skilled in the art.  
9 Preferred leaving groups are chloride and methylsulfate.  
10 Preferred alkylating agents include benzyl chloride,  
11 methyl chloride, alpha-chloroacetic acid, dimethyl  
12 sulfate, and alpha-chloromethyl phosphoric acid.  
13  
14 It is preferable to react all of the amine nitrogens with  
15 the derivatizing agent, although partial derivatization  
16 can occur. The ratio of alkylating agent to  
17 polyalkylenepolyamine nitrogen can be from 20:1 to 0.05:1  
18 on a molar basis; more preferably the ratio is from 2:1 to  
19 1:1.  
20  
21 In one embodiment the present invention is a composition  
22 containing derivatives of polyalkylenepolyamines  
23 comprising mixtures of (i) at least one C-alkyl-ethylene  
24 diamine polyammonium salt and (ii) at least one di-(C-  
25 alkyl)-diethylenetriamine polyammonium salt. Here each C-  
26 alkyl group on the ethylene diamine and the  
27 diethylenetriamine independently contains between 8-26  
28 carbon atoms. These polyammonium salts have more than one  
29 of the nitrogens of each of the derivatized  
30 polyalkylenepolyamines having a positive charge;  
31 preferably substantially all the nitrogen atoms of both  
32 components (i) and (ii) are positively charged. It is  
33 preferred to have polyammonium salts -- salts with more  
34 than a single positive charge. These  
35 polyalkylenepolyamine derivatives are also be described as  
36 polyderivatized.

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1 Preferred derivatized products include alkylation products  
2 of alkyl halides and sulfates with N-methylated  
3 polyalkylene polyamines.

4

5 More preferred derivatized products include (1) the  
6 products obtained by the reaction of benzyl chloride with  
7 N-methylated C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>, and C<sub>20-24</sub> polyalkylene  
8 polyamines and mixtures thereof; (2) the products obtained  
9 by the reaction of methyl chloride with N-methylated C<sub>10</sub>,  
10 C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>, and C<sub>20-24</sub> polyalkylenepolyamines and  
11 mixtures thereof; (3) the products of the reaction of  
12 dimethyl sulfate with N-methylated C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>,  
13 and C<sub>20-24</sub> polyalkylenepolyamines and mixtures thereof; (4)  
14 the products of the reaction of alpha-chloromethyl  
15 phosphoric acid with C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>, and C<sub>20-24</sub>  
16 polyalkylenepolyamines and mixtures thereof; and (5) the  
17 products obtained by the reaction of alpha-chloromethyl  
18 phosphoric acid with N-methylated C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>, and  
19 C<sub>20-24</sub> polyalkylenepolyamines and mixtures thereof.  
20 Especially preferred products are prepared from C<sub>12</sub>, C<sub>14</sub>, or  
21 C<sub>16</sub> polyalkylenepolyamines, more preferably from C<sub>14</sub> and C<sub>16</sub>  
22 polyalkylenepolyamines.

23

24 Mixtures of polyalkylenepolyamines having more than one  
25 carbon number can be used as the starting material; for  
26 example, mixtures of C<sub>10</sub> polyalkylenepolyamines with C<sub>14</sub>  
27 polyalkylenepolyamines are useful corrosion inhibitors  
28 when derivatized. Preferred derivatives are extremely  
29 dispersible or soluble in water, making them effective  
30 corrosion inhibitors in substantially aqueous media.

31

32 2. Alkoxylation of the Polyalkylenepolyamines

33

34 A second method for obtaining a polyalkylenepolyamine  
35 derivative of this invention is to react a  
36 polyalkylenepolyamine mixture containing Structures 1 and  
37 2 with an alkylene oxide. Alkoxylation of amines is well

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1 known in the art. Typical reaction conditions include  
 2 temperature in the range of 80-100°C and elevated  
 3 pressure. This reaction produces a mixture of at least  
 4 one N-alkoxylated C-alkyl-ethylenediamine and at least one  
 5 N-alkoxylated di-(C-alkyl)-diethylenetriamine.

6

7 An N-alkoxylated C-alkyl-ethylenediamine of this invention  
 8 is exemplified by Structure 5 below.

9

10

11

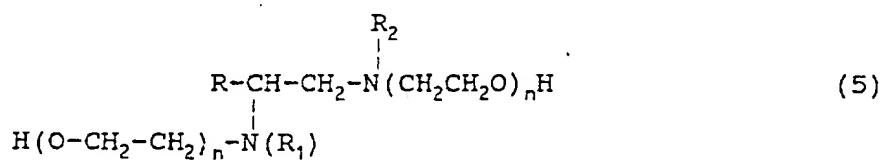
12

13

14

15

16



17

In Structure 5, R is an alkyl group containing 8 to 26 carbon atoms. R<sub>1</sub> and R<sub>2</sub> individually can be any combination of hydrogen and lower alkyl groups. Each n is independently between 0 and 4, with the sum of all n's being at least 1.

22

An N-alkoxylated di-(C-alkyl)-diethylenetriamine is described by a modified version of Structure 2, in which some or all of the R<sub>3</sub>, R<sub>8</sub> and R<sub>9</sub> groups are ethoxy or polyethoxy, (CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H, and each n is independently between 0 and 4, with the sum of all n's being at least 1.

28

In one embodiment the present invention is a composition containing derivatives of polyalkylenepolyamines comprising a mixture of (i) at least one C-alkyl-ethylene diamine poly-N-ethoxylate and (ii) at least one di-(C-alkyl)-diethylenetriamine poly-N-ethoxylate. Here each C-alkyl group on the ethylene diamine and the diethylenetriamine independently contains between 8-26 carbon atoms. In these poly-N-ethoxylated compositions, at least one of the nitrogens of each of the derivatized polyalkylenepolyamines has an ethoxy group (n=1) or a polyethoxy group (n>1), e.g., in the (-CH<sub>2</sub>-CH<sub>2</sub>-O-)<sub>n</sub>-H

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1 group of structures. Preferably substantially all the  
2 nitrogen atoms of both components (i) and (ii) are  
3 ethoxylated or polyethoxylated. These  
4 polyalkylenepolyamine derivatives can also be described as  
5 poly-derivatized.

6

7 Preferred ethoxylation agents are alkylene oxides such as  
8 ethylene oxide and propylene oxide; ethylene oxide is most  
9 preferred. The ratio of alkoxylation agent to amine  
10 nitrogen in the polyalkylenepolyamine can be in the range  
11 of from 100:1 to 0.5:1. Preferably it is in the range of  
12 from 10:1 to 1:1, more preferably 8:1 to 2:1. The amount  
13 of amine nitrogen is based on the total amine content of  
14 the polyalkylenepolyamine.

15

16 The derivatized, water-soluble polyalkylenepolyamine  
17 composition consists of a mixture containing: (a) at  
18 least one N-alkoxylated C-alkyl-ethylene diamine as  
19 described in Structure 5 and (b) at least one N-  
20 alkoxylated di-(C-alkyl)-diethylenetriamine as described  
21 hereinabove. Each C-alkyl group in the derivatized  
22 ethylene diamine and diethylenetriamine independently  
23 contains from 8-26 carbon atoms.

24

#### 25 Corrosion Inhibition

26

27 Some of the derivatized polyalkylenepolyamine compositions  
28 of this invention have turned out to be surprisingly good  
29 corrosion inhibitors in heavily aqueous media. Because  
30 they are dispersible in the aqueous layer which is usually  
31 in direct contact with the corrodible metals or metal  
32 alloys, they demonstrate superior performance over other  
33 commercially-available, hydrocarbon-soluble, corrosion  
34 inhibitors. These compositions are particularly effective  
35 at inhibiting the corrosion which can occur on oil  
36 drilling rods and in underground pipelines used to  
37 transport oil.

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1 The ability of these derivatized polyalkylenepolyamine  
2 compositions to act as effective corrosion inhibitors in  
3 these situations rests in part on the length of the alkyl  
4 group associated with each of the individual derivatized  
5 compounds. As has been noted in detail throughout this  
6 application, the alkyl groups which are part of our  
7 derivatized polyalkylenepolyamines are relatively long  
8 chains containing from 8 to 26 carbon atoms. Preferably,  
9 these chains will be between 8 and 16 carbons in length,  
10 more preferably between 10 and 14 carbon atoms.

11

12 Not wishing to be bound by any theory, it is believed that  
13 the length of the alkyl group affects the corrosion  
14 inhibition properties of the derivatized  
15 polyalkylenepolyamines. The nitrogen atoms which are part  
16 of these derivatized compounds are relatively polar and  
17 have been found to adhere to the potentially affected  
18 metal alloy. The long chain alkyl groups essentially form  
19 a "tail" which is very lipophilic in nature. When enough  
20 derivatized polyalkylenepolyamines are present, the  
21 hydrophobicity of these alkyl "tails" acts as a barrier  
22 and prevents corrosive oxygen and sulfur molecules from  
23 attacking the metal. Short alkyl chains on these  
24 polyalkylenepolyamines do not provide the coverage  
25 necessary to give effective corrosion inhibition.

26

27 In standard wheel tests using NACE brine at 90°C tested in  
28 saturated CO<sub>2</sub> solution, various formulations of the  
29 derivatized polyalkylenepolyamine compositions of this  
30 invention provided at least 85% corrosion inhibition at  
31 125 ppm of inhibitor. Most often, these compositions  
32 provided greater than 90% corrosion inhibition. These  
33 same compounds also demonstrated dispersibility ratings  
34 under 10 rating units as determined by the Water  
35 Dispersibility Test using NACE Brine as outlined in  
36 Example 12. It is the combination of these two factors

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1 which ensures effective corrosion inhibition in heavily  
2 aqueous environments.

3

4 The instant invention also relates to methods for using  
5 the derivatized polyalkylenepolyamine compositions as  
6 effective corrosion inhibitors. It is preferred to  
7 deliver the derivatized compositions to the potentially  
8 affected metal surface in a continuous process at a  
9 concentration ranging from 1 ppm - 1000 ppm, preferably  
10 from 5 ppm - 200 ppm, and most preferably between 10 ppm -  
11 100 ppm. Batch delivery in larger doses is also  
12 acceptable.

13

14 For use as corrosion inhibitors, the derivatized  
15 polyalkylenepolyamines of the invention are applied to the  
16 metal surfaces to be protected in a variety of ways known  
17 in the art. For example, a dilute aqueous solution of the  
18 derivatized polyalkylenepolyamine may be contacted with  
19 the metal to be protected, using methods such as dipping,  
20 spraying, wiping, and the like. For this method of  
21 application, solutions of about 0.1 to 10%, preferably  
22 from about 0.2 to 1%, by weight of derivatized  
23 polyalkylenepolyamine, or mixtures of derivatized  
24 polyalkylenepolyamine and other active corrosion  
25 inhibiting agents, are employed.

26

27 Alternatively, water-dispersible formulations of the  
28 present derivatized polyalkylenepolyamines, or mixtures of  
29 the derivatized polyalkylenepolyamines and other active  
30 corrosion inhibiting agents, can be added to a corrosive  
31 aqueous environment. In this method of application,  
32 sufficient amounts of derivatized polyalkylenepolyamines,  
33 or mixtures of the derivatized polyalkylenepolyamines and  
34 other active corrosion inhibiting agents, are added to  
35 give from about 1 to 1,000 ppm, preferably from 10 to 200  
36 ppm, of active corrosion inhibitor in the final solution  
37 for continuous methods of treatment. For batch treatment

1 methods, the level of corrosion inhibiting agents is  
2 generally between 500 and 25,000 ppm, preferably between  
3 500 and 5,000 ppm.

4

5 Generally, corrosion inhibitors are formulated with other  
6 components for corrosion inhibiting application.

7 Preferably, the corrosion inhibiting derivatized  
8 polyalkylenepolyamine composition of the present invention  
9 will be combined with one or more dimer/trimer acids to  
10 provide a formulated product. Dimer/trimer acids are  
11 well-known in the art and are typically derived from fatty  
12 acids. Examples of dimer/trimer acids include Empol 1024,  
13 Empol 1041 and Empol 1052, obtained from Emery Chemicals.

14

15 In addition to the derivatized polyalkylenepolyamine of  
16 the invention and the dimer/trimer acid, corrosion  
17 inhibiting formulations may also contain one or more  
18 surfactants, one or more alcohols, a small amount of a  
19 hydrocarbon and water. The surfactant employed may be  
20 ionic or nonionic in nature. The hydrocarbon may be any  
21 of the known solvents, such as kerosene, high aromatic  
22 distillate, diesel fuel, paint thinner, toluene,  
23 lubricating oil, and similar materials. A typical  
24 hydrocarbon is kerosene. Isopropanol or methanol are  
25 typical alcohols useful as solvents. Formulations  
26 containing at least 20 wt % water and/or alcohol are  
27 preferred.

28

29 Generally, the active corrosion inhibiting agents will be  
30 combined with a solvent and a surface-active agent to  
31 produce a concentrated solution of the corrosion  
32 inhibitor. In this solution, the derivatized  
33 polyalkylenepolyamine, or mixture of the derivatized  
34 polyalkylenepolyamine and other active corrosion  
35 inhibiting agents, will be present in amounts ranging from  
36 about 10 to 60%, preferably about 30 to 50%, by weight.  
37 The amount of solvent present is from about 30 to 80%, and

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1 the amount of surfactant is about 1 to 20%, by weight.  
2 This concentrated formulation is then diluted to the  
3 desired concentration of the final solution.  
4  
5 A typical water-dispersible formulation will contain about  
6 15 to 30% of the present derivatized  
7 polyalkylenepolyamine, about 15 to 30% of a dimer/trimer  
8 acid, about 1 to 10% of a nonionic surfactant, about 0 to  
9 10% of a hydrocarbon solvent, such as kerosene, and about  
10 10 to 40% of an alcohol, such as isopropanol or methanol.  
11  
12 Water-dispersible formulations of the present derivatized  
13 polyalkylenepolyamines are particularly useful in brine/CO<sub>2</sub>  
14 or brine/H<sub>2</sub>S environments, such as encountered in oil  
15 wells, especially oil wells employing secondary oil  
16 recovery techniques.  
17  
18 The following examples illustrate the basic principles of  
19 this invention. They are not to be construed as limiting  
20 the invention in any way except as indicated by the  
21 appended claims.  
22  
23   EXAMPLES  
24  
25   Example A  
26   MEASUREMENT OF TOTAL AMINE VALUE (TAV)  
27  
28 Total Amine Value (TAV), or Total Base Number (TBN) was  
29 measured using an ORION 960 autochemistry system sold by  
30 Orion Research Inc. The method is described in the Orion  
31 960 Instruction Manual (1988) using the Gran function and  
32 technique 10. The TAV is the quantity of acid, expressed  
33 in term of the equivalent number of mg of KOH, that is  
34 required to neutralize all basic constituents present in 1  
35 g of sample.

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### Example B

## NITROGEN CONTENT

The weight percent nitrogen is determined using a Carlo Erba 1500 Nitrogen Analyzer. Nitrogen compounds were converted to nitrogen gas and detected with a thermal conductivity detector. Samples were weighed into a tared tin cup which was crimped and placed in an autosampler. The sample was dropped into a heated tube and totally combusted with oxygen over copper oxide and Cr<sub>2</sub>O<sub>3</sub> catalysts. The combustion gases and helium carrier gas were swept through a reduction tube filled with copper metal fines to reduce nitrogen oxides to nitrogen gas. Water, and carbon dioxide were then scrubbed using 3A molecular sieves and ascarite. The remaining gas passed through a gas chromatographic column. The total amount of nitrogen was calculated by assuming that peak area is proportional to amount of nitrogen. Weight percent nitrogen in the sample was found by dividing the total amount of nitrogen by the sample weight.

21

## Example 1 - Procedures For Preparing Starting Materials

23

24 Outlined below are the typical procedures used to prepare  
25 polyalkylenepolyamine and methylated polyalkylenepolyamine  
26 compositions which serve as the starting materials for the  
27 compositions of this invention. Examples 1A to 1F  
28 describe useful methods of preparing these starting  
29 materials.

30

31 Examples 2-11 exemplify methods for making specific  
32 polyalkylenepolyamine derivatives. These procedures can  
33 readily be modified by those skilled in the art for  
34 polyalkylenepolyamines having different carbon numbers.

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1                           Example 1A

2                           PREPARATION OF C<sub>10</sub> POLYALKYLENEPOLYAMINE

3

4     To a 1-liter autoclave equipped with an air-drive stirrer  
5     250 g of C<sub>10</sub> epoxide (prepared from a decene heartcut), 38  
6     g of wet Raney Nickel catalyst, and 16 cc of distilled  
7     water were added to 450 cc of liquid ammonia and 40 psig  
8     of hydrogen.

9

10   The mixture was stirred at 1500 rpm for 45 minutes until  
11   the composition reached 185°C. This temperature was  
12   maintained with stirring for 2.5 hours. The maximum  
13   pressure during the reaction was 2800 psig. The  
14   composition was then cooled to a temperature of 100°C  
15   while stirring at 150 rpm. Excess ammonia was vented and  
16   the product was filtered to remove catalyst. A semisolid  
17   waxy amine product (243 g) was obtained. Structure of the  
18   product was confirmed by NMR. The product had a TAV of  
19   367, and a DSC endpoint of 152°F.

20

21   Polyalkylenepolyamines of other carbon chain lengths were  
22   prepared from the corresponding epoxides using this  
23   procedure and adjusting the amounts charged to maintain a  
24   10:1:1 mole ratio of ammonia/epoxide/water, while ensuring  
25   a maximum 75% autoclave fill factor at room temperature.

26

27   Raney Nickel is not a particularly active amination  
28   catalyst; usually 6-10 wt% based on the amount of epoxide  
29   in the reactor is used. The solid catalyst should be well  
30   dispersed during production of the polyalkylenepolyamines  
31   giving good suspensions of the catalyst.

32

33                           Example 1B

34                           PREPARATION OF C<sub>14</sub> POLYALKYLENEPOLYAMINE

35

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1 The procedure of Example 1A was followed using 290.3 g of  
2 a C<sub>14</sub> epoxide. The procedure yielded 314 g of a C<sub>14</sub>  
3 polyalkylenepolyamine as the product.

4

5                   Example 1C

6                   PREPARATION OF N-METHYLATED C<sub>10</sub> POLYALKYLENEPOLYAMINE

7

8 To 60 g of the C<sub>10</sub> polyalkylenepolyamine of Example 1A,  
9 placed in a 1000 ml 3-necked round bottom flask sitting in  
10 an ice bath, 189.6 g of 98% formic acid was slowly added  
11 with constant stirring. The mixture was then removed from  
12 the ice bath. To this mixture, 185.4 ml of 37%  
13 formaldehyde solution was added. This new mixture was  
14 then heated at reflux (100-110°C). After approximately 10  
15 minutes, carbon dioxide began to form. Once the evolution  
16 of carbon dioxide subsided, the reaction mixture was  
17 heated continuously at 100°C for 16 hours.

18

19                   Example 1D

20                   FIRST PREPARATION OF N-METHYLATED C<sub>14</sub> POLYALKYLENEPOLYAMINE

21

22 A C<sub>14</sub> polyalkylenepolyamine was prepared as in Example 1B.  
23 To 150 g of this C<sub>14</sub> polyalkylenepolyamine, in a 2000 ml 3-  
24 necked round bottom flask sitting in an ice bath, 400 g of  
25 98% formic acid was slowly added with constant stirring.  
26 The mixture was then removed from the ice bath and 500 g  
27 of 37% formaldehyde solution was added. This new mixture  
28 was then heated at reflux (100-110°C). After  
29 approximately 10 minutes, carbon dioxide began to form.  
30 Once the evolution of carbon dioxide subsided, the  
31 reaction mixture was heated continuously at 100°C for 16  
32 hours. After cooling to room temperature, excess reagent  
33 was removed under reduced pressure. The oily residue was  
34 dissolved in conc. HCl and washed with toluene. The  
35 aqueous layer was then basified with conc. NaOH and  
36 extracted with toluene. The toluene was evaporated to

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1 yield 158 g of a brown liquid product. The structure of  
2 the product was confirmed by IR and NMR spectra.

3

4                   Example 1E

5                   SECOND PREPARATION OF N-METHYLATED  
6                   C<sub>14</sub> POLYALKYLENEPOLYAMINE

7

8 A C<sub>14</sub> polyalkylenepolyamine was prepared as in Example 1B.  
9 A 50 g of this C<sub>14</sub> polyalkylenepolyamine (6.6% of N), and  
10 19.55 g of 98% formic acid was mixed in 200 ml 3-neck  
11 flask equipped with stirrer and condenser. The mixture  
12 was heated to 100°C. To this mixture 12.33 g of solid  
13 paraformaldehyde was added batchwise so that the  
14 liberation of carbon dioxide was controlled at a  
15 manageable rate. After carbon dioxide evolution subsided,  
16 the reaction mixture was heated at 100-110°C for 8 hours.  
17 The mixture was then cooled to room temperature and  
18 diluted with 200 ml of toluene (or diethyl ether), and the  
19 organic solution was washed with 100 ml of 5% aqueous  
20 sodium hydroxide. The organic layer was dried (MgSO<sub>4</sub>), and  
21 solvent was removed in vacuo to give 70 g of an oily  
22 product. The structure of product was confirmed by IR and  
23 NMR spectra. The meltpoint, i.e., second DSC endpoint,  
24 for this product is 123°F.

25

26                   Example 1F

27                   PREPARATION OF N-METHYLATED AND  
28                   C<sub>16</sub> POLYALKYLENEPOLYAMINES

29

30 A C<sub>16</sub> polyalkylenepolyamine was prepared from the C<sub>16</sub>  
31 epoxide in a manner similar to Example 1A. The produce  
32 had a meltpoint (DSC endpoint of 194°F. This produce was  
33 methylated as in Example 1E. The DSC endpoint of this  
34 produce was 109°F. As this example shows, the methylated  
35 produce had a substantially lower meltpoint than the  
36 starting polyalkylenepolyamine.

37

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1                   Example 2A

2                   PREPARATION OF C<sub>10</sub> POLYALKYLENEPOLYAMINE  
3                   REACTION PRODUCT WITH ALPHA-CHLOROMETHYL PHOSPHORIC ACID

4  
5     A mixture of 20 g of the C<sub>10</sub> polyalkylenepolyamine of  
6     Example 1A (9.17 wt% N, 0.131 eq.), and 18.8 g of alpha  
7     chloromethyl phosphoric acid in 100 ml of methyl t-butyl  
8     ether solvent was heated at reflux (80°C) for 30 hours  
9     under nitrogen. On removal of solvent it gave 36.5 g of a  
10    brown viscous oil, which soon became a glassy solid.  
11    Total Amine Value (TAV) analysis was consistent with the  
12    expected structure. The dispersibility and corrosion  
13    inhibition properties demonstrated by this product are  
14    outlined in Table 1, Run 20.

15

16                   Example 2B

17                   PREPARATION OF C<sub>14</sub> POLYALKYLENEPOLYAMINE  
18                   REACTION PRODUCT WITH ALPHA-CHLOROMETHYL PHOSPHORIC ACID

19  
20    The procedure of Example 2A was followed using the  
21    N-methylated C<sub>14</sub> polyalkylenepolyamine of Example 1D or 1E.  
22    The structure was checked by NMR and TAV analysis. The  
23    dispersibility and corrosion inhibition properties  
24    demonstrated by this product are outlined in Table 1 Run  
25    35.

26

27                   Example 3

28                   PREPARATION OF C<sub>10</sub> POLYALKYLENEPOLYAMINE  
29                   REACTION PRODUCT WITH PHOSPHOROUS ACID AND FORMALDEHYDE

30

31    To a mixture of 20 g of C<sub>10</sub> polyalkylenepolyamine (9.17 wt  
32    % N, 0.131 eq.), 12.99 ml (21.45 g, 0.262 mole) of  
33    phosphorous acid, and 21.23 ml of formaldehyde (37%, 0.262  
34    mole) in a 3 neck round bottom flask, 52.32 ml of  
35    concentrated HCl was added dropwise. The reaction was  
36    slightly exothermic. After the addition of HCl, the  
37    mixture was heated at 100°C for 5 hours. Aqueous work up

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1 and evaporation gave a solid product of mp 75-88°C. The  
2 structure was checked by NMR and TAV analysis. The  
3 dispersibility and corrosion inhibition properties  
4 demonstrated by this product are outlined in  
5 Table 1, Run 21.

6

7                   Comparative Example 4

8                   PREPARATION OF C<sub>10</sub> POLYALKYLENEPOLYAMINE  
9                   REACTION PRODUCT WITH DIMETHYL CARBONATE

10

11 Twenty (20) ml of dimethyl carbonate was added to a  
12 solution of 20 g of C<sub>10</sub> polyalkylenepolyamine (9.17% of N,  
13 0.131 eq.), in 100 ml of anhydrous isopropyl alcohol. The  
14 reaction mixture was heated at reflux under nitrogen  
15 atmosphere for 48 hours. After removal of solvent in  
16 vacuum, 34 g of yellow brownish solid was obtained. TAV  
17 of product was 123.04 (TAV of starting amine was 367).  
18 The dispersibility of this product was poor, see Table 1,  
19 Run 22. This product is not a good water-dispersible  
20 corrosion inhibitor.

21

22                   Example 5A

23                   PREPARATION OF C<sub>12</sub> POLYALKYLENEPOLYAMINE  
24                   REACTION PRODUCT WITH DIMETHYL SULFATE

25

26 A mixture of 20 g of a C<sub>12</sub> polyalkylenepolyamine (8.15%  
27 of N) prepared in the manner of Example 1A, and 15.41 g  
28 (0.1223 mole) of dimethyl sulfate was dissolved in 100 ml  
29 of anhydrous isopropyl alcohol. The mixture was heated at  
30 reflux under nitrogen gas for 5 hours. On removal of  
31 solvent it yielded 29.4 g of amber glassy product.  
32 Product was checked by NMR and TAV analysis. The  
33 dispersibility and corrosion inhibition properties  
34 demonstrated by this product are outlined in Table 1, Run  
35 25.

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1                           Example 5B

2                           PREPARATION OF C<sub>14</sub> POLYALKYLENEPOLYAMINE  
3                           REACTION PRODUCT WITH DIMETHYL SULFATE

4  
5     The procedure of Example 5A was followed using the  
6     N-methylated C<sub>14</sub> polyalkylenepolyamine of Example 1D or 1E.  
7     Product was checked by NMR and TAV analysis. The  
8     dispersibility and corrosion inhibition properties  
9     demonstrated by this product are outlined in Table 1, Run  
10    35.

11                          Example 6

12                          PREPARATION OF C<sub>14</sub> POLYALKYLENEPOLYAMINE  
13                          REACTION PRODUCT WITH BENZYL CHLORIDE

14  
15    A mixture of 20 g of C<sub>14</sub> polyalkylenepolyamine (6.99%  
16    of N, 0.099 eq.), and 13.28 g of benzyl chloride (0.105  
17    mole) in 100 ml of isopropyl alcohol was heated at reflux  
18    for  
19    15 hours. Reaction was monitored with reverse phase thin  
20    layer chromatography (TLC). After completion of reaction,  
21    solvent was removed under vacuum. It gave 30.48 g of a  
22    viscous liquid. Structure was confirmed by IR, NMR, and  
23    Total Amine Value analysis (=zero). The dispersibility  
24    and corrosion inhibition properties demonstrated by this  
25    product are outlined in Table 1, Run 26.

26

27                          Example 7A

28                          PREPARATION OF C<sub>16</sub> POLYALKYLENEPOLYAMINE  
29                          REACTION PRODUCT WITH METHYL CHLORIDE

30

31    A solution of 20 g of C<sub>16</sub> polyalkylenepolyamine (TAV=240),  
32    in 80 ml of isopropyl alcohol was placed in an autoclave.  
33    To this solution 9.68 g (100% excess) of methyl chloride  
34    was charged. The mixture was heated at 100°C with 500 psi  
35    of nitrogen pressure for 10 hours with vigorous stirring.  
36    Reaction was monitored with reverse phase TLC. After  
37    removal of solvent and excess methyl chloride, 23.35 g of

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1 solid product was obtained, mp >250°C. Product was  
2 checked by NMR and TAV (= 6). The corrosion inhibition  
3 properties demonstrated by this product are outlined in  
4 Table 1, Run 29.

5

6 Example 7B

7 PREPARATION OF C<sub>14</sub> POLYALKYLENEPOLYAMINE  
8 REACTION PRODUCT WITH METHYL CHLORIDE

9

10 The procedure of Example 2A was followed using the N-  
11 methylated C<sub>14</sub> polyalkylenepolyamine of Example 1C or 1D.  
12 Results Table 1 Run 35.

13

14 Comparative Example 8

15 PREPARATION OF C<sub>20-24</sub> POLYALKYLENEPOLYAMINE  
16 REACTION PRODUCT WITH CHLOROACETAMIDE

17

18 A mixture of 20 g of C<sub>20-24</sub> polyalkylenepolyamine (4.8%  
19 N, 0.0685 eq.), and 6.55 g (0.07 mole) of chloroacetamide  
20 in 100 ml of toluene was heated at reflux under nitrogen  
21 for  
22 52 hours. After cooling to room temperature, the solid  
23 precipitates were filtered and dried in a vacuum oven  
24 (50°C). It yielded 16.5 g of product, mp 75-120°C; TAV =  
25 16.9, with 7.32% nitrogen. The dispersibility of this  
26 product is poor, see Table 1, Run 32. This product was  
27 not a good water dispersible corrosion inhibitor.

28

29 Example 9A

30 PREPARATION OF C<sub>10</sub> POLYALKYLENEPOLYAMINE  
31 REACTION PRODUCT WITH ETHYLENE OXIDE

32

33 A mixture of 25 g of C<sub>10</sub> polyalkylenepolyamine (10% of  
34 nitrogen, 0.178 eq.), 7.86 g of anhydrous ethylene oxide  
35 (0.178 eq.), 40 ml of acetonitrile, and 40 ml of t-butyl  
36 methyl ether was charged into a 100 ml autoclave cooled by  
37 dry ice and acetone bath. The mixture was heated to 86°C

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1 and vigorously stirred for 4 hours. The autoclave was  
2 cooled to room temperature and vented. The mixture was  
3 placed on the rotatory evaporator to remove solvents. It  
4 yielded 30 g of brown oil as product (TAV=174, 6.82% of  
5 N). The product was tested as a corrosion inhibitor  
6 without further purification. The dispersibility and  
7 corrosion inhibition properties demonstrated by this  
8 product are outlined in Table 1, Run 23.

9

10                           Example 9B  
11                           PREPARATION OF C<sub>10</sub> POLYALKYLENEPOLYAMINE  
12                           REACTION PRODUCT WITH 10 ETHYLENE OXIDE EQUIVALENTS  
13

14 A mixture of 25 g of C<sub>10</sub> polyalkylenopolyamine, (10% of  
15 nitrogen, 0.178 eq.), prepared in the manner as described  
16 in Example 1A, 78.6 g of anhydrous ethylene oxide (1.78  
17 eq.), 1 ml of trifluoracetic acid, 200 ml of acetonitrile,  
18 and 100 ml of t-butyl methyl ether is charged into a 500  
19 ml autoclave cooled by a dry ice/acetone bath. The  
20 mixture is heated to 86°C and vigorously stirred for 4  
21 hours. The autoclave is cooled to room temperature and  
22 vented. The liquid is then placed on a rotatory  
23 evaporator and yields a brown oily product. This product  
24 is an effective corrosion inhibitor.

25

26                           Example 10A  
27                           PREPARATION OF C<sub>10</sub> N-METHYLATED POLYALKYLENEPOLYAMINE  
28                           REACTION PRODUCT WITH BENZYL CHLORIDE  
29

30 A mixture of 20 g of C<sub>10</sub> N-methylated polyalkylenopolyamine  
31 (9.61% of N, 0.137 eq.) prepared in Example 1B, and 18.24  
32 g of benzyl chloride (0.144 mole) in 100 ml of isopropyl  
33 alcohol was heated at reflux for 15 hours. Reaction was  
34 monitored with reverse phase TLC. After completion of  
35 reaction, solvent was removed under vacuum. It gave 34.4  
36 g of a brownish, oily, liquid product. Structure was  
37 confirmed by IR, NMR, and TAV analysis (=zero). The

-30-

1 dispersibility and corrosion inhibition properties  
2 demonstrated by this product are outlined in Table 1, Run  
3 24.

4

5                   Example 10B

6 FIRST PREPARATION OF C<sub>14</sub> N-METHYLATED POLYALKYLENEPOLYAMINE  
7                   REACTION PRODUCT WITH BENZYL CHLORIDE

8

9 A mixture of 15 g of C<sub>14</sub> N-methylated polyalkylenepolyamine  
10 (7.14% of N, 0.0765 eq.) prepared in Example 1C, and 9.68  
11 g of benzyl chloride (0.0765 eq.) in a solution of 80 ml  
12 t-butyl methyl ether and 20 ml of acetonitrile was heated  
13 at reflux for 15 hours. Reaction was monitored with  
14 reverse phase TLC. After completion of reaction, solvent  
15 was removed under vacuum. It gave 20 g of a brownish,  
16 oily, viscous product. Structure was confirmed by IR,  
17 NMR, and TAV analysis (which was zero). Product was  
18 checked by NMR and TAV analysis. The dispersibility and  
19 corrosion inhibition properties demonstrated by this  
20 product are outlined in Table 1, Run 34.

21

22                   Example 10C

23 SECOND PREPARATION OF C<sub>14</sub> N-METHYLATED  
24                   POLYALKYLENEPOLYAMINE REACTION PRODUCT  
25                   WITH BENZYL CHLORIDE

26

27 A mixture of 25 g of C<sub>14</sub> N-methylated polyalkylenepolyamine  
28 (5.49% of N, 0.098 eq.) preparation in Example 1E, and  
29 11.17 g of benzyl chloride (0.088 eq.) in a solution of 50  
30 ml of isopropyl alcohol was heated at reflux for 15 hours.  
31 Reaction was monitored with reverse phase TLC. After  
32 completion of reaction, solvent was removed under reduced  
33 pressure. It gave 36 g of viscous oil as product.  
34 Structure was confirmed by IR, NMR, and TAV analysis  
35 (which was zero).

36

-31-

1 After cooling to room temperature, excess reagent was  
2 removed under reduced pressure. The oily residue was  
3 dissolved in conc. HCl and washed with toluene. The  
4 aqueous layer was then basified with conc. NaOH and  
5 extracted with toluene. The toluene was evaporated to  
6 yield 64.5 g of a brown oily product. The structure of  
7 the product was confirmed by IR and NMR spectra. Product  
8 was checked by NMR and TAV analysis. The dispersibility  
9 and corrosion inhibition properties demonstrated by this  
10 product are outlined in Table 2, Run 34.

11

12                   Example 11

13                   BENZYL CHLORIDE QUATS OF METHYLATED AMINES

14

15 Additional benzyl chloride quats were prepared from a  
16 methylated C<sub>16</sub> polyalkylenepolyamine (to give a quat having  
17 14 carbon atoms in the alkyl group side chain) and from a  
18 methylated C<sub>20-24</sub> polyalkylenepolyamine (to give a quat  
19 having 18 to 22 carbon atoms in the alkyl group side  
20 chain).

21

22                   TABLE 2

23

24                   PERCENT CORROSION PROTECTION AT 50 PPM

25

No. of Carbons in Alkyl Group	Methylated Amine	Benzyl Chloride Quat
8	96.8	96.1
12	90.4*	95.8
14	79.2*	97.2
18-22	-	95.0

32

33 \* Run at 1000 PPM conc. instead of 50 PPM (as 50  
34 PPM was too low a level to observe corrosion  
35 protection for these amines).

36

37

38 Table 2 above summarizes the results for the continuous  
39 wheel test using polyalkylenepolyamines having a variety

-32-

1 of carbon atoms in the alkyl group. (Note: a C<sub>14</sub>  
2 polyalkylenopolyamine produces a quat with 12 carbon atoms  
3 in the alkyl group). As can be seen, the benzyl chloride  
4 quats of these methylated amines are excellent corrosion  
5 inhibitors at very low concentrations (50 ppm).

6

7                   Example 12

8                   WATER DISPERSIBILITY TEST USING NACE BRINE

9

10 The water dispersibility test evaluates the dispersibility  
11 of corrosion inhibitor formulations used in water-based  
12 environments. Each formulation's dispersibility behavior  
13 was monitored for 24 hours in standard NACE Brine at a  
14 90:10 ratio of brine to corrosion inhibitor formulation.  
15 The observations were tabulated so that the quality of the  
16 dispersions could be rated and compared on a numeric  
17 scale. The lower the rating, the more dispersible the  
18 formulation in aqueous environments.

19

20 In running this test, 45 ml of NACE Brine (which consists  
21 of 365.6 g of NaCl, 15.4 g of CaCl<sub>2</sub>, and 7 g of MgCl<sub>2</sub> per  
22 liter of water) was added to a 50 ml closed-top graduated  
23 cylinder.

24

25 Five ml of formulation consisting of 10% corrosion  
26 inhibitor in isopropyl alcohol was then added to the NACE  
27 Brine. If the formulation dispersed immediately, it was  
28 given a rating of zero.

29

30 If the formulation did not immediately disperse, the  
31 mixture was inverted once. It was noted whether the  
32 formulation dispersed in the NACE Brine at this point. If  
33 it failed to do so, the cylinder was inverted an  
34 additional 30 times and observed for any signs of  
35 dispersibility.

-33-

1    Each sample which had to be inverted was monitored after  
2    both 10 minutes and 24 hours to check for phase  
3    separations. Specifically, it was ascertained whether any  
4    cream layers, oil layers, or flocculation formulations  
5    were present. If so, the level of each layer (in ml) was  
6    measured. A cream layer is a milky or opaque combination  
7    of the oil and brine phases and could be twice the volume  
8    of the originally added formulation. An oil layer  
9    appeared as a clearly defined oil phase separated out on  
10   top of the brine or cream layer. Flocculation was  
11   observed as a separation of solid material and could be  
12   present in either a cream layer or oil layer.

13

14   The numeric ratings used to evaluate the formulation's  
15   dispersibility were based upon each sample's behavior at  
16   three time categories during the test.

17

- 18        A) Phase Behavior Upon Immediate Dissolution.
- 19        B) Phase Behavior After 10 Minutes.
- 20        C) Phase Behavior After 24 Hours.

21

22   At each stage, the solutions could exhibit the following  
23   four types of properties: 1) good dispersions (i.e., one  
24   phase either clear or opaque); 2) cream layer formation;  
25   3) oil layer formation; or 4) flocculation formation. The  
26   overall rating scale combines the individual  
27   dispersibility results obtained at each of the three  
28   stages. It is rated heavily against flocculation and oil  
29   layer formation, the most telling signs of a lack of  
30   dispersibility.

31

32   A) Immediate Dissolution Calculation

	<u>Rating Units</u>	<u>Comments</u>
35	0	Self-disperses
37	2	One turn dispersion, one phase after 24 hours

38

39

-34-

16 Note: There are a maximum of 12 Rating Units at this  
17 stage.

18

19 B) 10-Minute Calculation

24  
25 Cream & Oil Formation: The maximum number of Rating Units  
26 for cream formation (10 Rating  
27 Units) added to 4 Rating Units for  
28 each ml of oil measured. If any  
29 oil is detected, even if it does  
30 not amount to 1 ml, 1 Rating Unit  
31 is added.

33 Flocculation: Any flocculation results in 50  
34 Rating Units.

35

### 36 C) 24-Hour Calculation

37

38           While it is important for a formulation to stay  
39           dispersed indefinitely, its behavior after 10  
40           minutes is more important. The 24-hour  
41           calculation is weighted to reflect this fact.

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1           The 24-hour evaluation was done the same way as  
2           the 10-minute evaluation -- except that the  
3           resulting number was then weighted by  
4           subtracting the 10-minute number from it and  
5           dividing by 2; that is,  $(24 \text{ Hr}-10 \text{ Min.})/2$ .  
6

7           Total Dispersion Calculation  
8

9           The total number of Rating Units for a given  
10          formulation are obtained by combining the individual  
11          numbers calculated individually for A, B, and C as  
12          detailed above. The lower the number, the better  
13          the dispersibility of the formulation in aqueous  
14          media.  
15

16           Example 13  
17          SAMPLE WATER DISPERSIBILITY TEST CALCULATION  
18

19          A sample formulation was tested which showed the following  
20          dispersion characteristics: 1) It did not disperse  
21          immediately and only went into solution after 30  
22          inversions; 2) It separated out after 10 minutes,  
23          revealing 3 ml of cream and 2 ml of oil; and 3) After 24  
24          hours it had 1 ml of cream and 3 ml of oil.  
25

26          Total Dispersion Calculation  
27

28          A)       Immediate Dissolution Calculation: 30 turn  
29          dispersion with separation in 10 minutes yields  
30          10 Rating Units  
31

32          B)       10-Minute Calculation  
33

34          Since cream and oil are both present after 10  
35          minutes we start with the base level of 10  
36          Rating Units. To this we add 4 Rating Units  
37          for each ml of oil present.

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1                   Therefore,

2                 10-Minute Scale =  $(2 \times 4) + 10 = \underline{18}$  Rating  
3                 Units

4

5 C)           24-hour Calculation

6

7                 We initially calculate the 24-hour number in  
8                 the same manner as the 10-minute number. Since  
9                 cream and oil are both present after 24-hours,  
10                we start with the base level of 10 Rating  
11                Units. To this we add 4 Rating Units for each  
12                ml of oil present.

13

14               Therefore, since 3 ml of oil are present:

15               24-hour Scale =  $(3 \times 4) + 10 = 22$  Rating Units

16

17               We then need to calculate the 24-hour weighted  
18               number by subtracting the 10-minute calculation  
19               and dividing by two.

20

21               24-hour weighted Number Scale:

22                $(22-18)/2 = \underline{2}$  Rating Units

23

24               Total Dispersibility Rating

25

26               Total Dispersibility = A+B+C =  $10+18+2 = \underline{30}$

27

Rating            Units

28

29               Table 1 below summarizes the Water Dispersibility Test  
30               results for the derivatized polyalkylenepolyamines which  
31               are the subject of this invention.

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1    Example 14  
2    WHEEL TEST EVALUATION OF DERIVATIZED  
3    POLYALKYLENEPOLYAMINES AS CORROSION  
4    INHIBITORS FOR CO<sub>2</sub> CORROSION  
5

6     The Wheel Test is an industry standard test procedure used  
7     to evaluate corrosion inhibitors. The test is described  
8     in the National Association of Corrosion Engineers (NACE)  
9     publication ID182. The procedures followed in this  
10   example are essentially the same as those described in the  
11   NACE publication and are discussed below.

12

13   The test fluid consisted of 98% synthetic brine as  
14   described in NACE publication ID182 and 2% deodorized  
15   kerosene. The brine was flushed with nitrogen, then  
16   saturated with CO<sub>2</sub> gas at room temperature.

17

18   Test coupons were 5 ml thick mild steel shimstock and were  
19   sandblasted in a ball mill and tared prior to use. The  
20   test coupon, test fluid, and inhibitor were placed in a  
21   7-oz. juice bottle taking care to avoid oxygen  
22   contamination. The inhibitor was added at a level of 125  
23   ppm. The bottles were capped and placed on a rotating  
24   wheel mounted in a 90°C oven for 24 hours.

25

26   Following the test, the coupons were removed from the  
27   bottles, rinsed with soap and water, dipped in 10%  
28   hydrochloric acid, and rinsed with water. A plastic wool  
29   pad was used to scrub any remaining corrosion products  
30   from the coupon, after which the coupon was rinsed, dried,  
31   and weighed to determine the weight loss. The percent  
32   corrosion inhibition provided by the inhibitor was  
33   calculated with reference to the weight loss of an  
34   uninhibited coupon, according to the following formula:

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$$\% \text{ Inhibition} = \frac{(\text{Uninhibited weight loss} - \text{Inhibited weight loss})}{\text{Uninhibited weight loss}}$$

5

6 Table 1 below summarizes the corrosion inhibition test  
 7 results for the derivatized polyalkylenepolyamines which  
 8 are the subject of this invention.

9

10 As can be seen by these results, the derivatized  
 11 polyalkylenepolyamine compositions which were found to be  
 12 most water soluble proved to be excellent corrosion  
 13 inhibitors.

14

15 TABLE 1 -- Results at 125 ppm

16

17 RUN NO.	18 REACTANTS	DISPERSIBILITY RATING	CORROSION
19 INHIBITION <sup>2,3</sup>			
<b>C<sub>10</sub> POLYALKYLENEPOLYAMINE</b>			
20 20	- ALPHA-CHLOROMETHYL PHOSPHORIC ACID	5	95
21 21	- PHOSPHOROUS ACID AND FORMALDEHYDE	5	96
22* 22*	- DIMETHYL CARBONATE	NOT DISPERSED	--
23 23	- ETHYLENE OXIDE	SLIGHTLY DISPERSED	87
<b>C<sub>10</sub> N-METHYLATED POLYALKYLENEPOLYAMINE</b>			
34 24	- BENZYL CHLORIDE	2	98
<b>C<sub>12</sub> POLYALKYLENEPOLYAMINE</b>			
38 25	- DIMETHYL SULFATE	4	94
<b>C<sub>14</sub> POLYALKYLENEPOLYAMINE</b>			
42 26	- BENZYL CHLORIDE	5	93
43 27	- DIMETHYL SULFATE	4	94
44 28	- ETHYLENE OXIDE	21	--
<b>C<sub>16</sub> POLYALKYLENEPOLYAMINE</b>			
48 29	- METHYL CHLORIDE	NOT MEASURED	96

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1        C<sub>20-24</sub> POLYALKYLENEPOLYAMINE  
2

3	30	- ETHYLENE OXIDE	20	--
4	31	- BENZYL CHLORIDE	6	97
5	32*	- CHLOROACETAMIDE	NOT	--

6        DISPERSIBLE

7        -----  
8 \* COMPARATIVE EXAMPLES  
9

10 1. At 1% for 24 hours per Examples 12 and 13.  
 11 2. Per Example 14 at 125 PPM.  
 12 3. If dispersibility was poor, meaningful corrosion inhibition data  
 13 could not be obtained.

14

15

16        TABLE 1A -- Results at 50 ppm  
17

18 RUN NO.	19 REACTANTS	DISPERSIBILITY RATING	CORROSION
---------------	--------------	--------------------------	-----------

20 INHIBITION<sup>2,3</sup>21        C<sub>14</sub> N-METHYLATED  
22        POLYALKYLENEPOLYAMINE  
23

25 34	- BENZYL CHLORIDE	<4	95
26 35	- ALPHA-CHLOROMETHYL PHOSPHORIC ACID	<4	93
27 36	- METHYL CHLORIDE	<4	95
28 37	- DIMETHYL SULFATE	<4	94

30

31

32

33 \* COMPARATIVE EXAMPLES  
34

35 1. At 1% for 24 hours per Examples 12 and 13.  
 36 2. Per Example 14 at 50 PPM.  
 37 3. If dispersibility was poor, meaningful corrosion inhibition data  
 38 could not be obtained.

39

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1 WHAT IS CLAIMED IS:

2

3 1. Derivatives of polyalkylenepolyamines useful as  
4 corrosion inhibitors in aqueous media, comprising:

5

6 a composition produced by reacting

7

8 a) a derivatizing agent, which is either an  
9 alkylating agent or an alkylene oxide; with

10

11 b) a starting polyalkylenepolyamine comprising a  
12 mixture of:

13

14 (i) at least one C-alkyl-ethylene diamine; and

15 (ii) at least one di-(C-alkyl)-  
16 diethylenetriamine;

17

18 wherein each C-alkyl group on the ethylene diamine  
19 and the diethylenetriamine independently contain  
20 between 8-26 carbon atoms;

21

22 thereby producing derivatized polyalkylenepolyamines.

23

24 2. The composition according to Claim 1 wherein said  
25 polyalkylenepolyamine derivatives are either water  
26 soluble or have a water dispersibility rating under  
27 10.

28

29 3. The composition according to Claim 1 wherein said  
30 polyalkylenepolyamine derivatives are amine salts.

31

32 4. The composition according to Claim 1 wherein said  
33 polyalkylenepolyamine derivatives are quaternary  
34 amine salts.

35

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- 1       5. The composition according to Claim 1 wherein said  
2                   starting polyalkylenepolyamines are N-methylated  
3                   polyalkylenepolyamines.
- 4
- 5       6. The composition according to Claim 1 wherein said  
6                   polyalkylenepolyamine derivatives have a corrosion  
7                   inhibition rating in aqueous media above 90%.
- 8
- 9       7. The composition according to Claim 1 wherein the  
10                  alkylating agent, BX, has B selected from the group  
11                  consisting of hydrogen, an alkyl or aryl group,  
12                  benzyl, or alkylcarboxylate and X selected from the  
13                  group consisting of a halogen, sulfonate, carbonate,  
14                  phosphonate or other correspondingly good anion.
- 15
- 16      8. The composition described in Claim 7 where the  
17                  alkylating agent is an alkyl halide.
- 18
- 19      9. The composition described in Claim 8 where the  
20                  alkylating agent is methyl chloride.
- 21
- 22      10. The composition described in Claim 8 where the  
23                  alkylating agent is benzyl chloride.
- 24
- 25      11. The composition described in Claim 8 where the  
26                  alkylating agent is alpha-chloroacetic acid.
- 27
- 28      12. The composition described in Claim 8 where the  
29                  alkylating agent is alpha-chloromethyl phosphoric  
30                  acid.
- 31
- 32      13. The composition described in Claim 7 where the  
33                  alkylating agent is dimethyl sulfate.
- 34
- 35      14. The composition described in Claim 7 where the  
36                  alkylating agent is a mixture of phosphorous acid and  
37                  formaldehyde.

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- 1 15. The composition of derivatized polyalkylenepolyamines  
2 according to Claim 1 or 4 wherein each C-alkyl group  
3 contains between 8 to 16 carbon atoms.  
4
- 5 16. The composition of derivatized polyalkylenepolyamines  
6 according to Claim 15 wherein said C-alkyl group  
7 contains 12 or 14 carbon atoms.  
8
- 9 17. The composition according to Claim 1 wherein said  
10 polyalkylenepolyamine derivatives are obtained by  
11 reacting the starting polyalkylenepolyamine mixture  
12 with an alkylene oxide.  
13
- 14 18. The composition described in Claim 17 where the  
15 reactant is ethylene oxide.  
16
- 17 19. A composition comprising a polyderivatized mixture  
18 of:  
19  
20 (i) at least one C-alkyl-ethylene diamine; and  
21  
22 (ii) at least one di-(C-alkyl)-diethylenetriamine;  
23  
24 wherein each C-alkyl group on the ethylene  
25 diamine and the diethylenetriamine  
26 independently contain between 8-26 carbon  
27 atoms.  
28
- 29 20. The composition of Claim 19 wherein substantially all  
30 the nitrogen atoms of said components (i) and (ii)  
31 are positively charged.  
32  
33

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1 21. A composition containing derivatives of  
2 polyalkylenepolyamines useful as corrosion inhibitors  
3 in aqueous media, comprising:

4

5 a mixture of:

6

7 (i) at least one C-alkyl-ethylene diamine  
8 polyammonium salt; and

9

10 (ii) at least one di(C-alkyl)-diethylenetriamine  
11 polyammonium salt;

12

13 wherein each C-alkyl group on the ethylene  
14 diamine and the diethylenetriamine  
15 independently contain between 8-26 carbon  
16 atoms.

17

18 22. The composition of Claim 21 wherein substantially all  
19 the nitrogen atoms of said components (i) and (ii)  
20 are positively charged.

21

22 23. A composition containing derivatives of  
23 polyalkylenepolyamines useful as corrosion inhibitors  
24 in aqueous media, comprising:

25

26 a mixture of:

27

28 (i) at least one C-alkyl-ethylene diamine poly-N-  
29 ethoxylate; and

30 (ii) at least one di-(C-alkyl)-diethylenetriamine  
31 poly-N-ethoxylate;

32

33 wherein each C-alkyl group on the ethylene  
34 diamine and the diethylenetriamine  
35 independently contain between 8-26 carbon  
36 atoms.

37

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- 1 24. The composition of Claim 23 wherein substantially all  
2 the nitrogen atoms of said components (i) and (ii)  
3 are ethoxylated.
- 4
- 5 25. A method of inhibiting corrosion of a corrodible  
6 metal wherein a corrosion inhibiting effective amount  
7 of the composition of polyalkylenepolyamine  
8 derivatives described in one of Claims 1, 19, 21 or  
9 23 is contacted directly with the potentially  
10 affected metal part.
- 11
- 12 26. A method of inhibiting corrosion of corrodible metal  
13 material used in oil field operations wherein a  
14 corrosion inhibiting effective amount of the  
15 composition of polyalkylenepolyamine derivatives  
16 described in one of Claims 1, 19, 21 or 23 is  
17 injected directly into the well being drilled.
- 18
- 19 27. A composition according to Claim 7 wherein the C-  
20 alkyl group contains 12 or 14 carbon atoms and the  
21 alkylating agent, BX, has B selected from the group  
22 consisting of lower alkyl or benzyl and X selected  
23 from the group consisting of chloride, bromide or  
24 methyl sulfonate.
- 25
- 26 28. A composition comprising N-methylated  
27 polyalkylenepolyamines which are useful for preparing  
28 compositions as described in Claim 1.

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US92/08036

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C23F 11/14  
 US CL :252/8.555, 8.554, 390,392; 422/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/8.555, 8.554, 390,392; 422/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 4,900,458 (SCHROEDER ET AL.), 13 FEBRUARY 1980, entire document.	1-22,25-28
Y	US,A, 3,349,032 (KRIEG), 24 OCTOBER 1967, see col. 2 lines 60-71, col. 3 lines 23-51.	1-22,25-28
Y	US,A, 3,200,106 (DICKSON, ET AL), 10 AUGUST 1965, See col. 3 lines 1-23	23-25
Y	US,A, 2,761,843 (BROWN), 04 SEPTEMBER 1956. See col. 3 lines 55-74.	1-22,25-28

Further documents are listed in the continuation of Box C.

See patent family annex.

Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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		"&" document member of the same patent family

Date of the actual completion of the international search

01 DECEMBER 1992

Date of mailing of the international search report

14 DEC 1992

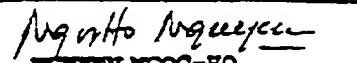
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